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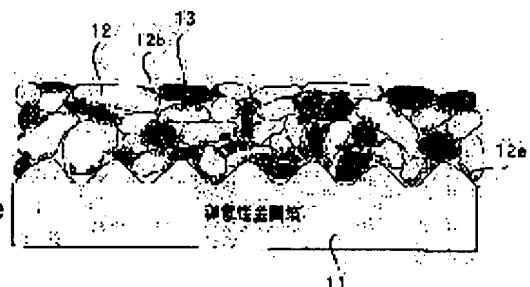
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(54) NEGATIVE ELECTRODE FOR LITHIUM SECONDARY BATTERY AND METHOD OF MANUFACTURING THE SAME

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a negative electrode for a lithium secondary battery capable of providing high service capacity and having excellent charge and discharge cycle characteristic and a method of manufacturing the same.

SOLUTION: The negative electrode is characterized that it is obtained by sintering mixture of active material 12, which contains silicon and/or silicon alloy, and conductive metal powder 13 on the surface of a collector 11, for which conductive metal foil is used, under reducing atmosphere.



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Notes:

1. Untranslatable words are replaced with asterisks (****).
2. Texts in the figures are not translated and shown as it is.

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CLAIMS

[Claim(s)]

[Claim 1] The negative electrode for lithium secondary batteries which uses conductive metal foil as a current collection object, and is characterized by being obtained by sintering the active material material containing silicon and/or a silicon alloy and the mixture of conductive metal powder under a reducing atmosphere on the surface of said current collection object.

[Claim 2] The negative electrode for lithium secondary batteries according to claim 1 characterized by having spread the metal component in said conductive metal foil and/or said conductive metal powder in said active material material.

[Claim 3] The negative electrode for lithium secondary batteries according to claim 1 or 2 characterized by surface roughness Ra of said conductive metal foil being 0.2 micrometers or more.

[Claim 4] Claim 1 characterized by being the atmosphere in which said reducing atmosphere contains hydrogen - the negative electrode for lithium secondary batteries given in any 1 clause of three.

[Claim 5] Claim 1 characterized by said conductive metal foil being a metallic foil which prepared electrolytic copper in electrolytic copper foil or the surface - the negative electrode for lithium secondary batteries given in any 1 clause of four.

[Claim 6] The active material material which contains silicon and/or a silicon alloy on the surface of conductive metal foil, and the process which arranges the mixture of conductive metal powder, The manufacture method of the negative electrode for lithium secondary batteries characterized by having the process which sinters said mixture under a reducing atmosphere in the state where it has arranged on the surface of said conductive metal foil.

[Claim 7] By applying slurry containing said active material material, said conductive metal powder, and a binder on the surface of said conductive metal foil The manufacture method of the negative electrode for lithium secondary batteries according to claim 6 characterized by arranging said active material material and said conductive metal powder on the surface of said conductive metal foil.

[Claim 8] The manufacture method of the negative electrode for lithium secondary batteries according to claim 6 or 7 characterized by surface roughness Ra of said conductive metal foil being 0.2 micrometers or more.

[Claim 9] The manufacture method of Claim 6 characterized by being the atmosphere in which said reducing atmosphere contains hydrogen - the negative electrode for lithium secondary batteries given in any 1 clause of eight.

[Claim 10] The manufacture method of the negative electrode for lithium secondary batteries given in Claim 6 characterized by said conductive metal foil being a metallic foil which prepared electrolytic copper in electrolytic copper foil or the surface - 9 any 1 clauses.

[Claim 11] The lithium secondary battery characterized by becoming a negative electrode given in Claim 1 - any 1 clause of five or Claim 6 - any 1 clause of ten from the negative electrode manufactured by the method of the description, the positive electrode containing positive active material, and nonaqueous electrolyte.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the negative electrode for lithium secondary batteries, its manufacture method, and a lithium secondary battery.

[0002]

[Description of the Prior Art] If a lithium metal is used for the negative electrode of a lithium secondary battery, high charge-and-discharge capacity can be obtained, but since a lithium metal deposits in the shape of a dendrite on a negative electrode in the case of charge, it has the problem of being easy to generate an internal short circuit etc.

[0003] It is possible to use lithium, such as Si, Sn, and aluminum, and the metal to alloy as negative electrode active material as what does not produce such a problem and can expect high charge-and-discharge capacity. However, if such a metal to alloy is used as an active material, high capacity is expectable, but there is a problem that an active material carries out pulverization and exfoliates from a current collection object by repetition of charge and discharge since the volume changes a lot.

[0004] In JP,H11-339777,A, after applying the slurry which contains silicon powder as an active material on a current collection object, reducing the contact resistance between a current collection object and an active material is proposed by calcinating this under a non-oxidizing atmosphere.

[0005]

[Problem to be solved by the invention] However, a charge-and-discharge cycle characteristic good enough could not be obtained by such a method, either, but there was a problem that it could not be considered as the practical negative electrode for lithium secondary batteries.

[0006] The purpose of this invention is related with the negative electrode for lithium secondary batteries which could obtain high charge-and-discharge capacity, and was excellent in charge-and-discharge characteristics, its manufacture method, and the lithium secondary battery using this.

[0007]

[Means for solving problem] The negative electrode for lithium secondary batteries of this invention uses conductive metal foil as a current collection object, and is characterized by being obtained by sintering the active material material containing silicon and/or a silicon alloy and the mixture of conductive metal powder under a reducing atmosphere on the surface of a current collection object.

[0008] [the manufacture method of the negative electrode for lithium secondary batteries of this invention] It is characterized by having the active material material containing silicon and/or a silicon alloy, the process which arranges the mixture of conductive metal powder, and the process which

makes this mixture sinter under a reducing atmosphere in the state where it has arranged on the surface of the above-mentioned conductive metal foil on the surface of conductive metal foil.

[0009] In the manufacture method of this invention, active material material and conductive metal powder are arranged on the surface of conductive metal foil by applying preferably slurry containing active material material, conductive metal powder, and a binder on the surface of conductive metal foil.

[0010] In this invention, active material material and the mixture of conductive metal powder are sintered under a reducing atmosphere on the surface of conductive metal foil. By heat-treating and sintering under a reducing atmosphere, the oxide layer of the surface of conductive metal foil and conductive metal powder is returned, and sintering between each of active material material, conductive metal foil, and conductive metal powder arises effectively. For this reason, the adhesion to the conductive metal foil, i.e., the current collection object, of active material material and conductive metal powder improves greatly. Therefore, the dilation and contraction with a big active material material which produce lithium in a charge-and-discharge reaction when emitting, occlusion and are controlled, and the exfoliation from the current collection object of the active material material by pulverization is also controlled.

[0011] Moreover, since conductive metal powder exists in the circumference of active material material, a firm conductive network is formed in the circumference of active material material. Therefore, current collection nature is raised and it can control that the contact resistance between active material material and a current collection object increases.

[0012] In this invention, it is desirable that surface roughness Ra uses the conductive metal foil which is 0.2 micrometers or more as a current collection object. The value of this surface roughness Ra is a value before sintering. Since the contact surface product on the mixture of active material material and conductive metal powder and the surface of a metallic foil becomes large by using the conductive metal foil which has such surface roughness Ra as a current collection object, Sintering under a reducing atmosphere takes place still more effectively, and the adhesion to the current collection object of active material material and conductive metal powder improves further. For this reason, the exfoliation from the current collection object of the dilation and contraction with a big active material which produce lithium in a charge-and-discharge reaction when emitting, occlusion and, and the active material by pulverization is controlled further.

[0013] Since it is desirable that it is in the range whose thickness of conductive metal foil is 10-100 micrometers so that it may be mentioned later, although the maximum in particular of surface roughness Ra of conductive metal foil is not limited, the maximum of surface roughness Ra is 10 micrometers or less substantially.

[0014] Moreover, as for the average interval S of surface roughness Ra and the local summit of the mountain, it is desirable to have the relation of $100 \text{ Ra} \geq S$. The average interval S of surface roughness Ra and the local summit of the mountain is provided in Japanese Industrial Standards (JIS B 0601-1994), for example, can be measured with a surface roughness meter.

[0015] As conductive metal foil used as a current collection object in this invention, the thing of the alloy which consists of metals or such combination, such as copper, nickel, iron, titanium, and Cobalt, for example can be mentioned. The thing containing the metallic element which is especially easy to diffuse in active material material is desirable. From such a viewpoint, it is desirable that it is copper

foil. It is easy to diffuse a copper element in active material material by heat treatment, and improvement in unity with the active material material in sintering can be expected. As copper foil whose surface roughness Ra is 0.2 micrometers or more, electrolytic copper foil is mentioned, for example. Electrolytic copper foil deposits copper with an electrolytic decomposition process on the surface of copper foil. Moreover, you may be the metallic foil of others in which copper by an electrolytic decomposition process was formed on the surface. As such a thing, what deposited copper with the electrolytic decomposition process can be mentioned to the surface of nickel foil. [0016] Moreover, in this invention, the thing of the same quality of the material as the above-mentioned conductive metal foil can be preferably used as conductive metal powder mixed with active material material. Specifically, it is the alloy which consists of metals or such combination, such as copper, nickel, iron, titanium, and Cobalt. Especially as conductive metal powder, copper powder is used preferably. By sintering active material material and the mixture of conductive metal powder under a reducing atmosphere on the surface of a current collection object The oxide of the surface of conductive metal foil and/or conductive metal powder is returned, the metal component produced as a result is spread in active material material, and it is thought that this metal component will be unevenly distributed around active material material. Since expansion contraction of the volume at the time of a charge-and-discharge reaction is controlled in the part where this metal component was unevenly distributed by using lithium, such as copper, and the metal component which is not alloyed as a metal component, Exfoliation of the active material from a current collection object and the pulverization of current collection object material should be controlled, and it should excel in the charge-and-discharge cycle characteristic.

[0017] Silicon and/or a silicon alloy are contained in the active material material used in this invention. As a silicon alloy, the eutectic alloy of the solid solution of silicon and one or more sorts of other elements, the intermetallic compound of silicon and one or more sorts of other elements, silicon, and one or more sorts of other elements etc. is mentioned. As the production method of an alloy, an arc melting method, a melt quenching method, the mechanical alloying method, the sputtering method, a chemical-vapor-deposition method, the calcinating method, etc. are mentioned. Especially as a melt quenching method, the various atomizing methods, such as a single chill roll method, a ** chill roll method and the gas atomizing method, the water atomizing method, and the disk atomizing method, are mentioned.

[0018] Moreover, as an active material material used in this invention, you may use what covered the grain surface of silicon and/or a silicon alloy with the metal etc. As the covering method, a nonelectrolytic plating method, the electrolysis plating method, chemistry reduction, vacuum deposition, the sputtering method, a chemical-vapor-deposition method, etc. are mentioned. It is desirable that it is the same metal as conductive metal foil or conductive metal powder as a metal which covers the grain surface. By covering the same metal as conductive metal foil and conductive metal powder, unity with the current collection object in the case of sintering and conductive metal powder can improve greatly, and the further excellent charge-and-discharge cycle characteristic can be obtained.

[0019] Although the mean particle diameter in particular of the active material material used in this invention is not limited, in order to produce effective sintering, it is desirable still more desirable that it is 100 micrometers or less, and it is 50 micrometers or less. Moreover, although the mean particle

diameter of the conductive metal powder used in this invention is not limited in particular, either, it is 50 micrometers or less that it is 100 micrometers or less desirable still more preferably.

[0020] As for the mixed rate of conductive metal powder, in this invention, it is desirable that it is within the limits of 0.05-50 to the active material material 1 in a bulk density. Since the mixed rate of active material material will decrease relatively if too large [if there are too few mixed rates of conductive metal powder, a good charge-and-discharge cycle characteristic may not be obtained, and], charge-and-discharge capacity becomes small.

[0021] In this invention, although the thickness in particular of conductive metal foil is not limited, it is desirable that it is the range of 10 micrometers - 100 micrometers. Moreover, although the thickness in particular of the sintered compact which consists of active material material on conductive metal foil and a mixture of conductive metal powder is not limited, 1000 micrometers or less are desirable still more desirable, and it is 10 micrometers - 100 micrometers.

[0022] Sintering under the reducing atmosphere in this invention is performed in the atmosphere of the gas which has reducing power, such as hydrogen and carbon monoxide, for example. As for the temperature of heat treatment at the time of sintering; it is desirable that it is the temperature below the fusing point of conductive metal foil, conductive metal powder, and active material material. For example, when copper is used as conductive metal foil and conductive metal powder, it is 400-800 degrees C that they are 1083 degrees C or less of fusing points desirable still more preferably. As a method of sintering, you may use discharge plasma sintering and the hot-press method.

[0023] The lithium secondary battery of this invention is characterized by consisting of the negative electrode manufactured by the negative electrode of above-mentioned this invention, or the manufacture method of above-mentioned this invention, a positive electrode containing positive active material, and nonaqueous electrolyte.

[0024] [the solvent of the electrolyte used for the lithium secondary battery of this invention] Although not limited in particular, the mixed solvent of cyclic carbonate, such as ethylene carbonate, propylene carbonate, and butylene carbonate, and chain-like carbonate, such as dimethyl carbonate, methylethyl carbonate, and diethyl carbonate, is illustrated. Moreover, the mixed solvent of said cyclic carbonate and ether system solvents, such as 1, 2-dimethoxyethane, 1, and 2-diethoxy ethane, is also illustrated. Moreover, LiPF₆, LiBF₄, and LiCF₃SO₃, as electrolytic solute, LiN(CF₃SO₂)₂, LiN(C₂F₅SO₂)₂, LiN(CF₃SO₂)(C₄F₉SO₂), LiC(CF₃SO₂)₃, and LiC(C₂F₅SO₂)₃ etc. -- and those mixtures are illustrated. Furthermore, inorganic solid electrolytes, such as the gel-like polymer electrolyte which sank the electrolyte into polymer electrolytes, such as polyethylene oxide and polyacrylonitrile, and LiI, Li₃N, are illustrated as an electrolyte. The electrolyte of the lithium secondary battery of this invention can be used without restrictions, unless the lithium compound as a solvent which makes ion conductivity discover, and the solvent which dissolves and holds this decompose on the voltage at the time of charge of a cell, discharge, or preservation.

[0025] As positive active material of the lithium secondary battery of this invention LiCoO₂, LiNiO₂, LiMn₂O₄, LiMnO₂, LiCo0.5nickel0.5O₂, and LiNi0.7Co0.2Mn0.1O₂ etc. -- a lithium content transition metal oxide and MnO₂ etc. -- the metal oxide which does not contain lithium is illustrated. Moreover, in addition to this, if it is the substance electrochemically intercalated and desorbed from lithium, it can use without restriction.

[0026] Drawing 2 is the typical sectional view showing an example of the negative electrode for

lithium secondary batteries of this invention. On the conductive metal foil 11, the active material material 12 and the conductive metal powder 13 are formed, and these are sintered under the reducing atmosphere. The field 12b which the metal component from Field 12a and the conductive metal powder 13 which the metal component from the conductive metal foil 11 diffused diffused is formed in the active material material 12. When the metal component diffused from the conductive metal foil 11 and the metal component diffused from the conductive metal powder 13 are lithium and a metal component which is not alloyed, in these diffusion fields 12a and 12b, expansion of the volume produced when the active material material 12 carries out occlusion of the lithium becomes small. Therefore, since the exfoliation from the conductive metal foil 11 of the active material material 12 and the exfoliation from the conductive metal powder 13 are controlled and the pulverization of active material material 12 self is also controlled further, it is thought that a charge-and-discharge cycle characteristic can be raised.

[0027]

[Mode for carrying out the invention] Although this invention is hereafter explained still in detail based on a working example, in the range which is not limited to the following working examples at all, and does not change the summary, it changes suitably and this invention can be carried out.

[0028] (Experiment 1)

[Production of a negative electrode] The weighing capacity of flake-like copper powder with a mean particle diameter [as conductive metal powder] of 10 micrometers and the silicon powder with a mean particle diameter [as an active material material] of 50 micrometers was carried out so that it might be set to 4:1 (=1:0.25) by a bulk density, and dry blending was carried out with the mortar. It mixed in 8weight % of N-methyl pyrrolidone solution containing the polyvinylidene fluoride 10 weight part as a binder, and this mixture 90 weight part was made into negative electrode mixture slurry.

[0029] Surface roughness Ra which is a current collection object applied this negative electrode mixture slurry to one side of the electrolytic copper foil (15 micrometers in thickness) which is 0.5 micrometer, and this was rolled after drying. What was obtained was clipped to 20mm in diameter disc-like, under a hydrogen atmosphere, this was heat-treated for 10 hours, was sintered 600 degrees C, and it was considered as the negative electrode. The thickness (a current collection object is not included) of the sintered compact was 50 micrometers.

[0030] [Production of a positive electrode] It is Li₂CO₃ as a starting material. And CoCO₃ It is under [air / after using, carrying out weighing capacity, mixing with a mortar so that the atomic ratio of Li:Co may be set to 1:1, and pressing and carrying out pressing of this by a metal pattern 17mm in diameter] setting. 800 degrees C is calcinated for 24 hours, and it is LiCoO₂. The calcination object was acquired. The mortar ground this and it prepared in mean particle diameter of 20 micrometers.

[0031] LiCoO₂ obtained With the powder 90 weight part, as an electric conduction agent, it mixed in 5weight % of N-methyl pyrrolidone solution containing the polyvinylidene fluoride 5 weight part as a binder, and the population graphite powder 5 weight part was made into positive electrode mixture slurry. This positive electrode mixture slurry was applied on the aluminium foil which is a current collection object, and it rolled, after drying. What was obtained was clipped to 20mm in diameter disc-like, and it was considered as the positive electrode.

[0032] [Production of an electrolyte] It is LiPF₆ to the constant volume mixed solvent of ethylene carbonate and diethylene carbonate as an electrolyte. What was dissolved 1mol/l. was produced.

[0033] [Production of a cell] The flat type lithium secondary battery A1 was produced using the above-mentioned positive electrode, the negative electrode, and the electrolyte. Drawing 1 is the cross section of the produced lithium secondary battery, and consists of a positive electrode 1, a negative electrode 2, a separator 3, the positive electrode can 4, the negative electrode can 5, the positive electrode current collector 6, a negative electrode current collection object 7, insulating packing 8 made from polypropylene, etc.

[0034] The positive electrode 1 and the negative electrode 2 have countered through a separator 3. These are stored in the cell case which the positive electrode can 4 and the negative electrode can 5 form. It connects with the positive electrode can 4 through the positive electrode current collector 6, a negative electrode 2 is connected to the negative electrode can 5 through the negative electrode current collection object 7, and the positive electrode 1 has structure in which the charge and discharge as a secondary battery are possible.

[0035] (Experiment 2) Nickel or copper was mixed with silicon so that it might be set to 9:1 by an atomic ratio, and Si9 Ni alloy and the Si9Cu alloy were produced with the single chill roll method. These alloys were ground so that it might become the mean particle diameter of 50 micrometers with a mortar. In the experiment 1, cells A2 and A3 were produced like the experiment 1 instead of silicon powder except using such after alloy powder. As for a cell A2, a cell A3 uses a Si9Cu alloy using Si9 Ni alloy.

[0036] (Experiment 3) The nonelectrolytic plating method covered the surface of silicon powder with a mean particle diameter of 50 micrometers with nickel. When checked with the atomic absorption method (ICP) about what was obtained, the amount of covering of the silicon powder by nickel was 0.5 weight % to the whole. In the experiment 1, the cell A4 was produced like the experiment 1 except using the silicon powder which covered this nickel instead of silicon powder.

[0037] (Experiment 4) With the electrolytic decomposition process, copper was deposited on the surface of nickel foil and stainless steel foil, and copper coating nickel foil (15 micrometers in thickness) and copper coating stainless steel foil (15 micrometers in thickness) were produced on it. Each of these surface roughness Ra was 0.5 micrometers.

[0038] In the experiment 1, cells A5 and A6 were produced like the experiment 1 instead of electrolytic copper foil except using such copper coating nickel foil and copper coating stainless steel foil. As for a cell A5, a cell A6 uses copper coating stainless steel foil using copper coating nickel foil. Moreover, the cell A7 was produced like the experiment 1 except surface roughness Ra using the electrolysis nickel foil which is 0.5 micrometer instead of electrolytic copper foil in experiment 1.

[0039] (Experiment 5) In the experiment 1, cells A8 and A9 were produced like the experiment 1 instead of flake-like copper powder except using flake-like nickel powder with a mean particle diameter of 10 micrometers or the flake-like iron powder end of 10-micrometer mean particle diameter. As for a cell A8, a cell A9 uses the end of flake-like iron powder using flake-like nickel powder.

[0040] Moreover, what mixed the flake-like copper powder used in the experiment 1 and flake-like nickel powder with a mean particle diameter of 10 micrometers with same weight was produced, and the cell A10 was produced like the experiment 1 except using this instead of flake-like copper powder in experiment 1.

[0041] (Experiment 6) In the experiment 1, except having made the heat treatment condition for

sintering into 600-degree-C 10 hours under argon atmosphere, the negative electrode was produced like the experiment 1 and the cell B1 was produced. Moreover, in the experiment 1, after applying negative electrode mixture slurry to electrolytic copper foil and drying and rolling, the negative electrode which did not perform heat treatment was produced and cell B-2 was produced like the experiment 1 using this.

[0042] [Evaluation of a charge-and-discharge cycle characteristic] The charge-and-discharge cycle characteristic was evaluated about the above-mentioned cells A1-A10, and B1 - B-2. In 25 degrees C, each cell was discharged to 2.7V with the electric current value of 1mA, after charging to 4.2V with the electric current value of 1mA, and this was made into the charge and discharge of 1 cycle. The number of cycles until it reaches 80% of the discharge capacity of 1 cycle eye was measured, and it was considered as cycle length. A result is shown in Table 1. In addition, the cycle length of each cell is the index which set cycle length of the cell A1 to 100.

[0043]

[Table 1]

電池	サイクル寿命
A 1 (水素雰囲気下)	100
A 2 (水素雰囲気下)	113
A 3 (水素雰囲気下)	120
A 4 (水素雰囲気下)	112
A 5 (水素雰囲気下)	99
A 6 (水素雰囲気下)	97
A 7 (水素雰囲気下)	99
A 8 (水素雰囲気下)	96
A 9 (水素雰囲気下)	92
A 10 (水素雰囲気下)	97
B 1 (アルゴン雰囲気下)	75
B 2 (熱処理なし)	15

[0044] The cell A1 heat-treated under a hydrogen atmosphere shows the outstanding cycle characteristic compared with the cell B1 heat-treated under argon atmosphere, and cell B-2 which did not perform heat treatment so that clearly from Table 1. By heat-treating under a hydrogen atmosphere, since the adhesion between copper foil, active material material, and copper powder improved further and current collection nature improved, this is considered.

[0045] (Experiment 7) Here, the relation between surface roughness Ra of a current collection object and a cycle characteristic was considered. In the experiment 1, the cell A11 and the cell A12 were produced like the experiment 1 except having used the rolled copper foil whose electrolytic copper foil

whose surface roughness Ra is 0.2 micrometer instead of and surface roughness Ra are 0.1 micrometer. [the electrolytic copper foil whose surface roughness Ra is 0.5 micrometer] About these cells, the cycle characteristic was evaluated like the above. In addition, cycle length is the index which set cycle length of the cell A1 to 100. The cycle length of a cell A1 is also collectively shown in Table 2.

[0046]

[Table 2]

電池	サイクル寿命
A 1 (表面粗さ Ra : 0. 5 μ m)	100
A 11 (表面粗さ Ra : 0. 2 μ m)	83
A 12 (表面粗さ Ra : 0. 1 μ m)	62

[0047] By the cells A1 and A11 using copper foil whose surface roughness Ra is 0.2 micrometers or more, it turns out that cycle length is long as compared with the cell A12 using copper foil with small surface roughness Ra so that clearly from Table 2. When surface roughness Ra uses a large metallic foil as a current collection object from these things, sintering between a metallic foil, active material material, and copper powder arises effectively, and is considered that adhesion improves.

[0048] (Experiment 8) Here, the relation between the mixed amount of conductive metal powder and a cycle characteristic was considered. In experiment 1, the silicon powder 1 is received by a bulk density in the mixed amount of flake-like copper powder. The cell A13, the cell A14, and the cell A15 were produced like the experiment 1 except having made it change so that it may be set to 1 (50 weight % of the amounts of copper powder), 0.5 (33.3 weight % of the amounts of copper powder), and 0.125 (11.1 weight % of the amounts of copper powder). Moreover, the cell B3 was produced like the experiment 1 as comparison except using only silicon powder, without mixing flake-like copper powder.

[0049] About these cells, the cycle characteristic was evaluated like the above. A result is shown in Table 3. In addition, the cycle length of each cell is the index which set cycle length of the cell A1 to 100.

[0050]

[Table 3]

電池	サイクル寿命
A 1 (銅粉末量 : 20 重量 %)	100
A 13 (銅粉末量 : 50 重量 %)	145
A 14 (銅粉末量 : 30. 3 重量 %)	124
A 15 (銅粉末量 : 11. 1 重量 %)	90
B 3 (銅粉末量 : 0 重量 %)	31

[0051] It turns out that the cell A1 which mixed flake-like copper powder, and A13-A15 show far good cycle length compared with the cell B3 which is not mixing flake-like copper powder so that clearly from Table 3. Since the adhesion of the silicon powder which is active material material by mixing

copper powder improves and the firm conductive network by copper powder is further formed in the surroundings of silicon powder, this is considered that current collection nature improved.

[0052]

[Effect of the Invention] According to this invention, it can be considered as the negative electrode for lithium secondary batteries and a lithium secondary battery excellent in the charge-and-discharge cycle characteristic.

[Translation done.]